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(54) Title: CATALYZED HYDROCARBON TRAP AND METHOD USING THE SAME		
(57) Abstract		
<p>A catalyst member suitable for catalyzing the oxidation to innocuous substances of gaseous hydrocarbons contained in an oxygen-containing exhaust stream is produced by disposing an adsorbent layer having a desorption temperature <math>T_D</math> on a carrier, and coating thereover a permeable catalytic layer having a light-off temperature <math>T_L</math>. Deleterious interaction between the adsorbent layer and the catalytic layer is avoided by the method of preparing the catalytic material of the catalytic layer and/or by disposing a barrier layer between the adsorbent layer and the catalytic layer. The preferred method for preparing the catalytic material includes impregnating a refractory support material with a solution containing dissolved salts of one or more platinum group metals, drying the wetted support material and fixing the platinum group metal(s) onto the support by thermal fixation, i.e., calcination, rather than chemical fixation, e.g., by exposure to gaseous <math>H_2S</math>. The barrier layer is preferably substantially free of silica and of platinum group metals. The catalytic layer contains a sufficient loading of one or more platinum group metals so that <math>T_L &lt; T_D + 150^\circ C</math>, e.g., there may be 300 grams or more of platinum group metals per cubic foot of the catalyst member.</p>		

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CATALYZED HYDROCARBON TRAP AND METHOD USING THE SAMEBACKGROUND OF THE INVENTION5 Field of the Invention

The present invention relates to an improvement in the treatment of engine exhaust gases utilizing a catalyst member that has an adsorbent material and a catalytic material. More particularly, the present invention relates to an improvement in long-term catalytic performance of such catalyst members.

10       Engines are fueled by hydrocarbonaceous fuels generally comprising gasoline or diesel fuel, but sometimes comprising alcohols, including ethanol and methanol, or mixtures of the above-mentioned fuels. The exhaust gas streams from such engines contain pollutants comprising hydrocarbons ("HC"), nitrogen oxides ("NO<sub>x</sub>") and carbon monoxide ("CO") which must be removed prior to discharging the exhaust gas stream into the atmosphere in order to comply with State and/or Federal Government  
15       exhaust emission standards. (Diesel exhaust contains solid particulates and, under certain conditions, liquid soluble oil fraction droplets in addition to gaseous components. However, for economy of expression, the terms "exhaust gas" or "gaseous stream(s)" as used herein and in the claims are intended to include diesel  
20       exhaust.) The problem of controlling the emission of pollutants, particularly hydrocarbons, is most acute during the cold-start period of engine operation, during which the engine and its exhaust gases are below normal operating temperatures and during which any catalyst used to convert the exhaust stream pollutants to innocuous substances, e.g., water and carbon dioxide, will be significantly below its optimum  
25       operating temperature. Generally, the cold-start period lasts for several minutes from the time an engine at ambient temperature is started, after which time the quantity of hydrocarbons in the exhaust gas is substantially reduced. A recognized industry procedure for measuring cold-start emissions is the Federal Test Procedure found at 40 CFR Part 86 Sections 115-178, and is commonly referred to as the FTP cold-start  
30       emissions test. Generally, this test involves starting an engine from a cold-start and measuring the emissions for a period of 505 seconds through various modes of engine operation, including idle, acceleration and deceleration.

Description of Related Art

U.S. Patent 5,510,086 to Hemingway et al, dated April 23, 1996, discloses an underfloor exhaust treatment device comprising three sequential catalyst members or "zones". The first zone comprises a delta alumina washcoat having platinum thereon, 5 preferably at a loading greater than 150 grams per cubic foot (g/ft<sup>3</sup>). The second zone comprises an adsorbent washcoat impregnated with more than 50 g/ft<sup>3</sup> palladium, and the third zone contains a refractory washcoat impregnated with 25-50 g/ft<sup>3</sup> of platinum and rhodium.

SAE paper 960796 by Chen et al, entitled "The Development of a Close 10 Coupled Plus Underfloor Catalyst for a ULEV Application", presented February 26, 1996, states that in tests on a 1990, 2.2 liter FTP vehicle fitted with a 1.4 liter underfloor catalyst having 300 gas flow passages per cross-sectional square inch ("cpsi"), catalytic hydrocarbon conversion performance was increased with increased 15 loading platinum group metal up to about 5.3 to 7.8 grams per liter Pt (150 to 220 g/ft<sup>3</sup>), above which adding more precious metal generated little improvement. Higher metal loadings, increased cell densities and various platinum group metal combinations were tested with mixed results.

U.S. Patent 5,078,979 to Dunne, dated January 7, 1992, discloses a process for 20 treating an engine exhaust gas stream, especially during cold start of the engine. The Patent discloses the use of a molecular sieve adsorbent bed upstream of a catalyst which serves to convert hydrocarbons and other pollutants contained in the gas being treated. The molecular sieve adsorbent bed is described (column 1, line 63 et seq) as 25 one having a Si:Al ratio of at least 24, as being hydrothermally stable and having a hydrocarbon selectivity greater than 1, i.e., of being more adsorbent of hydrocarbons than of water. Typical molecular sieve materials include zeolite Y, ultra stable zeolite Y and ZSM-5. As disclosed, starting at column 7, line 29, one or more catalytic metals, e.g., platinum, palladium, rhodium, ruthenium and mixtures thereof, may be 30 optionally dispersed onto the adsorbent in amounts of from 0.01 to about 4 weight percent of the adsorbent support (see column 7, lines 50 through 56). When the adsorbent is deposited on a honeycomb carrier, the carrier volume varies from about 1 to 3 liters, and the loading of adsorbent varies from about 100 to 450 grams (see column 7, lines 9 through 16).

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Japanese Patent Publication J02056247-A (90.02.26) of Toyota Jidosha KK discloses a catalyst used to remove hydrocarbons, carbon monoxide and nitrogen oxides from combustion exhausts which comprises a layer of zeolite over which is formed a catalyst layer comprising alumina on which 1.5 grams per liter of platinum (42.5 g/ft<sup>3</sup>), 0.3 grams per liter (8.5 g/ft<sup>3</sup>) of rhodium, 0.3 mols per liter of lanthanum and 0.3 mols per liter of cerium were loaded.

Japanese Patent Document S63-231178, based on application number S63-119728, filed May 17, 1988, discloses an exhaust treatment catalyst having a zeolite undercoat and a catalytic top coat. The amount of noble metal in the top coat is stated to be 0.1 to 10 grams per liter (about 2.8 to 283 g/ft<sup>3</sup>). This document teaches that increasing the loading of precious metal above 283 g/ft<sup>3</sup> does not yield significant improvement in catalytic performance.

SAE Paper 930738 by Engler et al, entitled "Reduction of Exhaust Gas Emissions by Using Hydrocarbon Adsorber Systems", dated March 1-5, 1993, discloses the concept of an exhaust gas treatment apparatus comprising an adsorbent and a catalyst wherein desorption occurs at temperatures exceeding the catalyst light-off (see part 2, page 8, column 2). However, there is no indication of how a catalytic material could be prepared to achieve such performance, and no indication that the adsorbent material and catalytic material could be disposed in the same catalyst member.

U.S. Patent 5,075,276, issued December 24, 1991 to M. Ozawa et al, discloses a catalyst containing ceria as an oxygen storage component which is said to be useful for purification of exhaust gases. The Ozawa et al catalyst comprises a support substrate on which is disposed a washcoat comprising (a) a high surface area material which may be alumina or titanium oxide, (b) cerium oxide, (c) zirconium oxide and (d) at least one oxide of a rare earth metal other than cerium and lanthanum (see column 3, lines 33-43). Noble metals such as platinum, palladium, rhodium, etc., and base metals such as chromium, nickel, vanadium, copper, cobalt, manganese, etc., are exemplified as catalytic metals to be utilized on the Ozawa et al TWC catalysts (column 3, line 58 et seq). The Ozawa et al composition is said to suppress thermal degradation of the oxygen storage component (column 2, lines 5-9) which would

otherwise occur unchecked, because of normal degradation of the ceria and consequent loss of surface area (column 1, lines 22-45).

### SUMMARY OF THE INVENTION

5 The present invention relates generally to the oxidation to innocuous substances of gaseous hydrocarbons contained in an oxygen-containing exhaust gas stream.

According to one broad aspect, the present invention provides a catalyst member suitable for catalyzing the conversion to innocuous substances of at least 10 gaseous hydrocarbons contained in an oxygen-containing exhaust stream. The catalyst member of this aspect of the invention comprises a refractory carrier, an adsorbent layer disposed on the carrier and comprising an adsorbent material for adsorbing hydrocarbons at temperatures up to a desorption temperature  $T_D$ , a permeable barrier layer disposed over the adsorbent layer, and a permeable catalytic 15 layer disposed over the adsorbent layer and the barrier layer and comprising a catalytic material effective at least for the conversion of hydrocarbons to innocuous substances.

According to a more specific aspect of the present invention, the barrier layer may comprise alumina, and it may comprise an oxygen storage component and/or a 20 stabilizer material, e.g., an alkaline earth metal oxide, or it may comprise both. The oxygen storage component may comprise bulk ceria and/or a co-formed oxide comprising ceria and an oxide of at least one other metal, e.g., zirconia. The co-formed oxide may comprise at least about 5 percent ceria by weight. For example, the co-formed oxide may comprise from 10 to 90 percent ceria by weight or, alternatively, 25 from about 10 to 50, or 10 to 40 or even 10 to 30 percent ceria by weight. The barrier layer may be substantially free of platinum group metals.

Yet another aspect of this invention provides that the catalyst member may have a light-off temperature  $T_L$  which is not more than about 150°C higher, preferably not more than about 50°C higher, than the desorption temperature  $T_D$ . Optionally, the 30 light-off temperature  $T_L$  may be not higher than the desorption temperature  $T_D$ , i.e.,  $T_L$  may be about the same as, or lower than,  $T_D$ .

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According to still another aspect of the invention, the catalytic material may comprise a platinum group metal component dispersed on a refractory metal oxide support material in an amount of at least about 100 grams, e.g., from about 200 to 700 grams, or, e.g., more than 300 grams, of platinum group metal per cubic foot of the catalyst member.

In a particular embodiment, the adsorbent layer may comprise a Beta-zeolite material having a Si:Al atomic ratio of at least about 100.

As used herein and in the claims, the desorption temperature ( $T_D$ ) is the temperature at which the adsorbent material in the adsorbent layer begins to show a net desorption of hydrocarbons. The light-off temperature ( $T_L$ ) is defined as the temperature at which the catalyst member attains fifty percent conversion performance, i.e., catalyzes the oxidation to innocuous substances of fifty percent of the hydrocarbon pollutants flowed therethrough.

As used herein and in the claims, the term "platinum group metals" means and includes ruthenium, rhodium, palladium, osmium, iridium and platinum.

Other aspects of the invention are described below.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a perspective view of a honeycomb-type refractory carrier member for use in accordance with one embodiment of the present invention;

Figure 1A is a partial cross-sectional view of the carrier member of Figure 1, enlarged relative to Figure 1 and taken along a plane parallel to the end faces of the carrier of Figure 1, showing a washcoat of material thereon;

Figure 1B is a partial cross-sectional view of a catalyst member according to one embodiment of the present invention, comprising the carrier member of Figure 1 in a view enlarged relative to Figure 1;

Figure 1C is a partial cross-sectional view of a catalyst member according to another embodiment of the present invention, showing a barrier layer between an adsorbent layer and a catalytic material layer; and

Figure 2 is a perspective view of an exhaust gas treatment apparatus comprising the catalyst member of Figure 1B.

**DETAILED DESCRIPTION OF THE  
INVENTION AND PREFERRED EMBODIMENTS THEREOF**

The present invention is particularly suited for lowering hydrocarbon emissions from an engine exhaust stream during the period of cold-start operation of 5 an internal combustion engine, and for converting noxious emissions thereafter.

The Applicants have discovered that in some layered catalysts, particularly of the type described in Japanese Application S63-119728 (discussed above), there is a significant loss of catalytic activity after the catalyst is aged. Without wishing to be bound by any particular theory, it is believed that the loss in activity is due to a 10 tendency for the platinum group metals of the catalytic top coat, during coating and aging, to migrate into the adsorbent material undercoat layer, i.e., into the zeolite, where a deleterious interaction between the platinum group metals and the zeolite adsorbent material occurs. Such migration occurs more readily in acidified, high silica zeolites than in non-acidified zeolites. In addition, migration of silica from the 15 zeolite into the top coat can occur, especially when the catalytic material is exposed to gas streams that contain steam and/or reductants such as hydrocarbons and/or carbon monoxide. The Applicants have discovered two methods for alleviating such migration.

Accordingly, the invention relates to flow-through catalyst members that 20 comprise a catalytic coating comprising at least an adsorbent layer and a catalytic layer. The adsorbent layer comprises an adsorbent material that serves to adsorb unburned hydrocarbons during the cold-start operating period and to retain them until the adsorbent material reaches its desorption temperature  $T_D$ . The catalytic layer comprises a catalytic material that serves to convert unburned hydrocarbons in the 25 exhaust gas stream, including those desorbed from the adsorbent material, to innocuous substances, e.g., to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Optionally, the catalytic material may also be effective for the conversion of carbon monoxide to innocuous substances, and/or the conversion of nitrogen oxides, e.g., to  $\text{N}_2$  and  $\text{O}_2$ . In the practice of the present invention, the catalytic layer is disposed over the adsorbent layer, so the 30 catalytic layer is sometimes referred to herein as a top coat and the adsorbent layer is sometimes referred to herein as an undercoat. Typically, the catalytic material comprises a catalytic species such as a platinum group metal component, i.e., at least

one platinum group metal. The platinum group metal component is dispersed on a support material comprising one or more relatively inert refractory oxides such as alumina, titania, etc. This invention provides improved long-term performance relative to other layered catalysts in that there is less migration of silicon from the adsorbent material into the catalytic material and/or less loss of platinum group metal from the catalytic material into the adsorbent material.

According to one aspect of this invention, a barrier layer is disposed between the adsorbent layer and the catalytic layer. Another aspect of the invention relates to the method by which the platinum group metals are fixed into the support material of the catalytic layer. Without wishing to be bound by any particular theory, it is believed that the two aspects of the present invention, which may be practiced independently, provide improved performance relative to prior art catalyst members by preventing migration of components of the adsorbent material into the catalytic material and/or preventing the loss of catalytically active species, i.e., platinum group metals, from the catalytic material into the adsorbent material, and thus inhibits deleterious interaction between them.

Ideally, the light-off temperature  $T_L$  of the catalytic material according to the present invention is not more than about 150°C higher than the desorption temperature  $T_D$  of the adsorbent material, so that desorption of adsorbed hydrocarbons does not begin until the catalytic material has become, or will soon become, effective for the oxidation of the desorbed hydrocarbons. In various embodiments,  $T_L$  may be not more than 130° greater than  $T_D$  or not greater than 100°C greater than  $T_D$ . Preferably, the light-off temperature  $T_L$  of the catalytic material is not more than about 50°C greater than  $T_D$ , since this will reduce the gap between  $T_D$  and  $T_L$  to a greater degree than has been achieved in the prior art. Even more preferably, a catalytic material of the present invention has a  $T_L$  that is not greater than, e.g., is about the same as, or is lower than,  $T_D$ . Since a typical desorption temperature  $T_D$  of the adsorbent material is about 120°C to 150°C, these limits, or the difference between  $T_L$  and  $T_D$ , indicate that catalytic materials of the present invention have a light-off temperature  $T_L$  that does not exceed about 250°C, which is lower than the light-off temperature of the prior art catalytic materials found in automobile catalysts. A typical light-off temperature  $T_L$  of the catalytic material of the present invention may be

about 210°C to 250°C (after aging of the catalyst), or it may be substantially lower, e.g., 175°C or 150°C, whereas most conventional catalytic materials have a light-off temperature of at least about 300°C. The low light-off temperature  $T_L$  is attained because of the very high loading of platinum group metal component in the catalytic material, as described more fully below. Preferably, the platinum group metal component principally comprises palladium, since palladium provides the most cost effective way to attain the desired  $T_L$ .

When  $T_L$  exceeds  $T_D$ , there will be a period of time when adsorbed hydrocarbons are being desorbed but are not being treated by the catalytic material to a significant degree. To ameliorate the consequence of such differences between  $T_L$  and  $T_D$ , the catalytic material may be maintained at a higher temperature than the adsorbent material so that the light-off temperature  $T_L$  is attained sooner than it otherwise would, and preferably before significant desorption of hydrocarbons from the adsorbent material takes place. Of course, this will also improve conversion performance if  $T_L$  is about the same as, or is lower than,  $T_D$ . Layering the catalytic material over the adsorbent material is a simple but preferred expedient for maintaining the catalytic material at a temperature higher than that of the adsorbent material because the layered arrangement causes the exhaust gas to contact the catalytic material before it contacts the adsorbent material. Therefore, the heat in the exhaust gas is imparted initially to the catalytic material, which will be heated more quickly to its light-off temperature than if the exhaust gas first contacted the adsorbent material, in which case the adsorbent material would adsorb heat from the exhaust gas, accelerating desorption and delaying the rise of the temperature of the catalytic material to the light-off temperature. Thus, heating the catalytic material before heating the adsorbent material reduces the time interval, if any, during which hydrocarbons are being desorbed before the catalytic material can effectively abate them.

The present invention is preferably used for the treatment of lean gas streams, i.e., those gas streams that contain more oxygen than is necessary to fully conduct the 30 carbonaceous species in the stream. For an engine (or other source) producing a stoichiometric gas stream, or even a rich gas stream, the oxygen content of the gas stream can be raised by injecting oxygen, or air, or another gaseous supply of oxygen,

into the gas stream or through the release of oxygen from an oxygen storage component in one or more of the layers of material.

The adsorbent material (sometimes referred to in the art as a "hydrocarbon trap" material) may comprise any material conventionally used to adsorb hydrocarbons, such as activated alumina, porous glass, silica gel and activated carbon. Natural and synthetic molecular sieves are particularly effective. Natural molecular sieves include faujasites, clinoptilolites, mordenites and chabazites. Zeolites, which comprise a class of molecular sieves which can be used, include silicalite, zeolite X, zeolite Y, ultra stable zeolite Y, ZSM-5, offretite and the like. Generally, sieve materials having so-called three-dimensional pore configurations are preferred over sieve materials having one- or two-dimensional pore configurations, although some of the latter function acceptably well. Zeolites, including Beta-zeolite, are preferred materials. Preferably, the zeolite material is a high silica material having a Si:Al atomic ratio of at least about 100:1 or greater. For example, the Si:Al ratio may be from about 100 to 200. Preferably, the Si:Al ratio is greater than about 170. A preferred adsorbent material comprises a zeolite that has been treated with an acid, such as sulfuric acid, to leach out aluminum atoms from the material and to thus raise the Si:Al ratio of the zeolite to that of a high silica zeolite. A high silica zeolite is preferred because it adsorbs less water than low silica zeolites, and so avoids coking hydrocarbons on the material surface.

As indicated above, one embodiment of the present invention relates to a catalytic coating comprising a barrier layer disposed between the catalytic layer and adsorbent layer. The barrier layer comprises a barrier material that serves as a physical barrier to inhibit the migration of platinum group metals from the catalytic layer into the adsorbent undercoat and of silicon (e.g., as silica) from the adsorbent layer into the catalytic layer. The barrier layer is permeable, however, to allow hydrocarbons to pass therethrough for adsorption by the adsorbent undercoat, yet it also acts as a thermal barrier that slows the rate at which the adsorbent material is heated by the exhaust gases and the exothermic activity of the catalytic material. The barrier layer comprises a barrier material which may comprise one or more refractory base metal oxides, e.g., alumina, preferably, a high surface area alumina, foamed alumina, ceria, ceria-zirconia, etc. Oxides of one or more rare earth metals such as

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lanthanum, yttrium, neodymium, and/or of one or more alkaline earth metals such as barium and/or strontium may be present in the barrier layer, e.g., as stabilizers for the alumina, zirconia or ceria. The stabilizer(s) may be admixed with the barrier layer material in bulk form or may be impregnated therein, and may be present in amounts of up to, e.g., about 30 percent of the combined weights of the barrier layer material and stabilizer.

The material of the barrier layer need not contain any significant amount of platinum group metals therein and it is preferably substantially free of platinum group metals, and it may advantageously be substantially free of silicon, e.g., as bulk silica or in silica-containing materials such as zeolites or other aluminosilicates, etc.

The barrier layer may be applied over the adsorbent layer in any conventional manner.

Optionally, the barrier material may comprise an oxygen storage component that adsorbs oxygen during periods of lean engine operation, e.g., fuel-cut mode, and releases oxygen during periods of rich engine operation, thus moderating diversions from stoichiometric engine operation. As described more fully below, oxygen storage components typically comprise rare earth metal oxides, e.g., ceria and/or solid solutions of ceria and zirconia. Alumina-stabilized ceria may also be used.

By disposing a substantially silicon-free barrier layer that is substantially free of platinum group metals between the adsorbent layer and the catalytic layer, migration of platinum group metals into the adsorbent layer is hindered, as is the migration of silicon into the catalytic layer. Thus, deleterious interactions between the platinum group metals and components of the adsorbent material such as silica, which would manifest themselves in loss of catalytic performance after aging, are hindered. Accordingly, the adsorbent material and catalytic material can be coated on the same carrier without deleterious loss of long term catalytic performance.

As mentioned above, the catalytic material of the present invention comprises a platinum group metal component deposited upon a refractory support material. The support material may comprise a high surface area alumina generally referred to in the art as "gamma alumina" or "activated alumina", which typically exhibits a BET surface area in excess of 60 square meters per gram ("m<sup>2</sup>/g"), often up to about 200 m<sup>2</sup>/g or more. Such activated alumina is usually a mixture of the gamma and delta

phases of alumina, but may also contain substantial amounts of eta, kappa and theta alumina phases. It is a known expedient in the art to stabilize such activated alumina supports against thermal degradation by the use of materials such as zirconia, titania, alkaline earth metal oxides such as baria, calcia or strontia or, most usually, rare earth metal oxides, for example, ceria, lanthana and mixtures of two or more rare earth metal oxides. For example, see C.D. Keith et al U.S. Patent 4,171,288. A variety of other support materials, e.g., ceria, alumina-stabilized ceria, zirconia, titania, etc., may be used, as is well-known in the art. The platinum group metal component may be disposed on the support in a conventional manner, e.g., a solution comprising a soluble salt of one or more platinum group metals may be impregnated into a powder comprising the support material to about 90% of incipient wetness. Water-soluble compounds or complexes, as well as organic soluble compounds or complexes, may be used. The only limitation on the liquids used to deposit these compounds, complexes, or elemental dispersions is that the liquids should not react with the metal compound and must be capable of being removed from the catalytic material by volatilization or decomposition by subsequent calcination and/or vacuum. Suitable compounds are, for example, palladium nitrate, palladium chloride, chloroplatinic acid, potassium platinum chloride, ammonium platinum thiocyanate, amine solubilized platinum hydroxide, rhodium chlorides, oxides, sulfides, nitrates, hexamine rhodium chloride and similar soluble decomposable compounds. The wetted support powder is then dried and the platinum group metal compound is fixed onto the support particles in catalytically active form.

One method for fixing the platinum group metal onto the support is chemical fixation, in which the impregnated support material is exposed to a strongly reducing environment, e.g., gaseous H<sub>2</sub>S. Another method is thermal fixation, in which, after the wetted support material is dried, it is then calcined, e.g., for an hour or more at 530°C, although the calcination temperature and duration may vary considerably, as is known in the art. Thermal fixation sometimes leads to less migration of platinum group metals into adsorbent materials as compared to chemical fixation. Thermal fixation is especially favored when the optional barrier layer is not used since the catalytic material will be fully in contact with the adsorbent material, and even more when the adsorbent material comprises an acidic zeolite, since acidic zeolites

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ordinarily induce more platinum group metal migration than non-acidified zeolites. Non-acidified zeolites are disfavored as adsorbents because they absorb more water and are therefore more prone to coking than acidified zeolites.

The catalytic material and the adsorbent material and, when employed, the

5 barrier material of the present invention are typically rendered in (or milled into) particulate form with particles in the micron-sized range, e.g., about 5 to 20 microns, e.g., 10 to 20 microns, in diameter, so that they can be formed into slurries and applied as washcoats onto carrier members, as is well-known in the art. Any suitable carrier member may be employed, such as a honeycomb-type carrier of the type

10 having a plurality of fine, parallel gas-flow passages extending therethrough from an inlet to an outlet face of the carrier, so that the passages are open to fluid-flow therethrough. The passages, which are typically essentially straight from their fluid inlet to their fluid outlet, are defined by walls on which the slurry is applied as a "washcoat" so that the gases flowing through the passages contact the material therein.

15 The flow passages of the carrier member are thin-walled channels which can be of any suitable cross-sectional shape and size such as trapezoidal, rectangular, square, sinusoidal, hexagonal, oval, or circular. Such structures may contain from about 60 to about 1200 or more gas inlet openings ("cells") per square inch of cross section ("cpsi"), more typically 200 to 600 cpsi. Such honeycomb-type carrier may be made

20 of any suitable refractory material, for example, it may be formed from a ceramic-like material such as cordierite, cordierite-alpha-alumina, silicon nitride, zirconium mullite, spodumene, alumina-silica magnesia, zirconium silicate, sillimanite, magnesium silicates, zirconium oxide, petalite, alpha-alumina and aluminosilicates. Alternatively, a honeycomb-type carrier may be made of a refractory metal such as

25 stainless steel or other suitable iron-based, corrosion-resistant alloys. The coated carrier is disposed in a canister configured to facilitate establishment of a gas flow path therethrough, as is known in the art and to protect it from damage from external forces. In yet other embodiments, the refractory carrier may comprise beads, pellets or particles (collectively referred to as "carrier beads") made of a suitable refractory

30 material such as gamma-alumina, which may be coated with the catalytic coating. A body of such carrier beads may be contained within a suitable perforated container which permits the passage of the exhaust gas therethrough. The carrier beads may be

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coated with both the adsorbent material, the catalytic material and, optionally, the barrier layer, in discrete respective layers.

As used herein and in the claims, the term "catalyst member" refers to a carrier onto which a catalytic coating, i.e., one comprising a layer of catalytic material, has 5 been applied.

A catalyst member according to the present invention is prepared by first 10 depositing the adsorbent material onto a refractory carrier to provide an adsorbent layer or undercoat. Optionally, a barrier material may be deposited over the adsorbent undercoat, to provide a barrier layer. Then, at least one layer of a catalytic material is deposited over the adsorbent layer and, when it is present, over the barrier layer, to 15 provide a catalytic layer or top coat. The catalytic layer and the optional barrier layer are permeable so that hydrocarbons in the exhaust gas that are not converted by the catalytic material can contact the undercoat to be adsorbed thereon, (especially during the cold-start period). The catalytic material can treat hydrocarbons later desorbed by the adsorbent material.

The adsorbent material, the optional barrier material and the catalytic material may be coated onto the carrier in any conventional manner. A common coating 20 technique comprises the preparation of a slurry (usually an aqueous slurry) comprising particles of the subject material and immersion of the carrier into the slurry, or spraying the slurry onto the carrier to coat the slurry thereon. The coated carrier is then dried, to remove the liquid component of the slurry, and is also usually calcined, leaving an adherent washcoat layer thereon.

Figure 1 shows a refractory "honeycomb"-type carrier 10 of generally 25 cylindrical shape having a cylindrical outer surface 12, one end face 14 and an opposite end face, not visible in Figure 1, which is identical to end face 14. The junction of outer surface 12 with the opposite end face at its peripheral edge portion is indicated at 14' in Figure 1. Carrier 10 has a plurality of fine, parallel gas flow passages 16 formed therein, better seen in enlarged Figure 1A. Gas flow passages 16 are formed by walls 18 and extend through carrier 10 from end face 14 to the opposite 30 end face thereof, the passages 16 being unobstructed so as to permit the flow of a fluid, e.g., a gas stream, longitudinally through carrier 10 via gas flow passages 16 thereof. A coating 20 is adhered to the walls 18 and, as shown in Figure 1A,

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comprises a plurality of layers of materials. In one embodiment of this invention, illustrated in Figure 1B, a catalyst member 22 according to the present invention comprises a carrier 10 which has thereon a first discrete layer 20a (sometimes referred to herein as an undercoat 20a) and a second discrete layer 20b (sometimes referred to herein as a top coat 20b) disposed over layer 20a. Undercoat 20a comprises adsorbent material, e.g., a high silica acidified zeolite material, and top coat 20b comprises a catalytic material according to the present invention, i.e., one comprising one or more platinum group metals dispersed on a support material such as activated alumina by the process of thermal fixation, described below. For purposes of illustration, the thickness of coating 20 and of layers 20a and 20b are exaggerated in Figures 1A and 1B.

In the embodiment of Figure 1C, catalyst member 22' comprises a carrier 10 on which a coating 20' has been disposed. Coating 20' comprises an adsorbent layer or undercoat 20a' and a catalytic layer or top coat 20b' with a barrier layer 20c' between them. Barrier layer 20c' inhibits migration of elements between the adsorbent material and the catalytic material, so when a barrier layer is used, the catalytic material of the catalytic layer need not be prepared using the thermal fixation process, although thermal fixation is preferably carried out even when a barrier layer is present.

When deposited onto a carrier, the amounts of the various catalytic components of the catalytic material are often presented based on grams per volume basis, e.g., grams per cubic foot ( $\text{g}/\text{ft}^3$ ) for platinum group metal components and grams per cubic inch ( $\text{g}/\text{in}^3$ ) for catalytic materials generally, as these measures accommodate different gas-flow passage sizes in different carriers, e.g., different cell sizes in honeycomb-type carriers. For typical automotive exhaust gas catalytic converters, the catalyst member generally comprises from about 0.5 to about 6  $\text{g}/\text{in}^3$ , preferably from about 1 to about 5  $\text{g}/\text{in}^3$  of catalytic material washcoat on the carrier.

To provide a suitably porous overlayer, the total loading of catalytic material overlying the adsorbent material preferably does not exceed about 5 grams per cubic inch ( $\text{g}/\text{in}^3$ ). For example, the catalytic layer may be applied at a loading of from about 2 to 4.5  $\text{g}/\text{in}^3$ , preferably about 3.0  $\text{g}/\text{in}^3$ . In addition to providing a permeable catalytic overlayer, the application of loadings of catalytic material in this range will

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avoid imparting a significant pressure drop in the exhaust gas flowing through the catalyst member.

Optionally, the catalytic material top coat may be applied as a series of two or more discrete layers of catalytic material disposed, one upon the next, over the 5 adsorbent material.

The adsorbent layer is typically coated onto the carrier substrate at a loading of 0.2 to 2 g/in<sup>3</sup>, e.g., 0.8 to 2 g/in<sup>3</sup>.

The barrier layer may be coated onto the carrier substrate at a loading of from about 0.1 to 3.0 g/in<sup>3</sup>, e.g., from about 0.2 to 2 g/in<sup>3</sup> or from about 0.5 to 1.5 g/in<sup>3</sup> or 10 even from about 0.8 to 1.2 g/in<sup>3</sup>, e.g., about 1g/in<sup>3</sup>.

As is well-known in the art, a catalyst member as shown in Figures 1A, 1B or 1C can be mounted in a canister as part of an exhaust gas treatment apparatus. For example, as shown in Figure 2, exhaust gas treatment apparatus 24 comprises a catalyst member 22' mounted in a canister 26 that has an inlet 28 to which an exhaust 15 gas line 30 from an engine exhaust manifold (not shown) can be connected, to provide gas flow communication between the engine and the catalyst member. Canister 26 has an outlet 32 that permits outflow from the outlet face of the catalyst member 22'. Typically, the outlet 32 is connected to a muffler to dampen engine noises before the exhaust gas is discharged to the atmosphere.

20 Generally, the catalytic material of the present invention functions as a "three-way conversion" catalyst suitable for catalyzing the conversion of hydrocarbons, carbon monoxide and nitrogen oxides in automotive exhaust gases to innocuous substances, e.g., H<sub>2</sub>O and N<sub>2</sub>. A "three-way conversion" catalyst is a term commonly used to refer to catalysts which are capable of substantially simultaneously 25 catalyzing oxidation of hydrocarbons and CO and reduction of nitrogen oxides. As is well-known in the art, three-way conversion activity is best achieved when an engine operates at or close to stoichiometric conditions. Three-way conversion catalysts typically comprise a platinum group metal component comprising at least one, and typically a plurality, of platinum group metals, e.g., one or more of platinum, 30 palladium and rhodium.

As mentioned above, the catalytic material of the present invention has a light-off temperature T<sub>L</sub> that is not more than about 150°C higher than, and is

preferably about the same as, or lower than, the temperature  $T_D$  at which the adsorbent material begins to desorb hydrocarbons. This is accomplished by incorporating into the catalytic material a higher loading of platinum group metals than was used in the prior art, to impart to the catalytic material a lower light-off temperature than that which is conventionally attained by three-way conversion catalysts. The uniquely high loading of platinum group metals must be achieved without requiring a loading of the catalytic material over the adsorbent material so heavy that the adsorbent material is obscured from exposure to the gas stream. Accordingly, the catalytic material is more highly loaded with platinum group metals, on a weight percent basis, than catalytic materials used in prior art catalysts. Typically, the catalytic material used in the present invention comprises at least about 0.5 weight percent platinum group metal by weight of the catalytic material in the top layer, measured as the metal. For example, the catalytic material may comprise from about 0.5 to 15 weight percent platinum group metals. By using such high weight percentages, the high loadings of platinum group metals needed on a weight per volume basis can be achieved without employing an excessive loading of the catalytic material layer. The platinum group metal component in a catalyst composition according to one aspect of the present invention is present in an amount of at least about 100 g/ft<sup>3</sup>, preferably, at a loading of from about 140 to 220 g/ft<sup>3</sup>, more preferably at a loading of from about 200 to 700 g/ft<sup>3</sup>. In some embodiments, the platinum group metal loading may be greater than 283 g/ft<sup>3</sup> (10 g/l), preferably greater than 300 g/ft<sup>3</sup>. The platinum group metal component may comprise one or more platinum group metals, e.g., palladium and one or both of platinum and rhodium. On a weight per volume basis, palladium may be used at 35 to 700 g/ft<sup>3</sup> in accordance with some embodiments of the present invention, but more typically 150-350 g/ft<sup>3</sup>. Preferably, the palladium loading is greater than 200 g/ft<sup>3</sup>, e.g., 210-350 g/ft<sup>3</sup>, more preferably, 225-350 g/ft<sup>3</sup>. Of course, the limits of the palladium loadings can be described in terms of any combination of these minimums and maximums, e.g., 35 to 350 g/ft<sup>3</sup>, 210-700 g/ft<sup>3</sup>, etc. Platinum is preferably used at a loading of 1-100 g/ft<sup>3</sup>, e.g., 1-50 g/ft<sup>3</sup>, preferably 5-30 g/ft<sup>3</sup>, e.g. about 20 g/ft<sup>3</sup>. Rhodium, when used is preferably used at a loading of 1-100 g/ft<sup>3</sup>, e.g., 1-50 g/ft<sup>3</sup>, more preferably at 5 to 50 g/ft<sup>3</sup>, e.g., about 8 g/ft<sup>3</sup>. When all three of

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these catalytic, platinum group metals are present, they are preferably present in a Pt:Pd:Rh ratio of about (1-3):(10-700):(1-2).

The catalytic material and/or the barrier layer may comprise one or more rare earth metal oxide promoters, which are generally known in the art, and which may be 5 in bulk form, that is, present as fine particles, e.g., 5 to 20 microns in diameter, e.g., 10 to 20 microns in diameter. For example, the rare earth metal oxide promoters in bulk form may be present as co-precipitated particles of two or more rare earth metal oxides. Alternatively, such promoters may be dispersed in the catalytic material by impregnating the latter with a solution of a soluble rare earth salt, such as a nitrate, 10 followed by calcination to convert the nitrate to the oxide. Such promoters may comprise ceria at a loading of about 0.1 to 1.5 g/in<sup>3</sup>; zirconia at a loading of up to 1.0 g/in<sup>3</sup>; neodymia at a loading of up to 0.4 g/in<sup>3</sup> or, alternatively, up to 0.2 g/in<sup>3</sup>; 15 lanthana at a loading of up to 0.4 g/in<sup>3</sup> or, alternatively, up to 0.2 g/in<sup>3</sup>; nickel oxide at a loading of up to 0.2 g/in<sup>3</sup> or, alternatively, up to 0.1 g/in<sup>3</sup>; iron oxide at a loading of up to 0.02 g/in<sup>3</sup> or, alternatively up to 0.05 g/in<sup>3</sup>; and baria and strontia at loadings of 20 up to 0.4 g/in<sup>3</sup>.

Bulk ceria is known to be a useful additive for such catalyst compositions, especially TWC compositions in which the bulk ceria is believed to serve as an oxygen reservoir and is sometimes referred to as an oxygen storage component 20 (OSC). It is believed that in treating, for example, the exhaust gas of an engine operating at air-to-fuel ratios which fluctuate slightly above and below stoichiometric, the ceria supplies additional oxygen for the oxidation reaction during rich (relatively oxygen-deficient) periods of operation and takes up oxygen during lean (relatively oxygen-rich) periods of operation. Bulk ceria is not, however, immune to the problem 25 of thermal degradation which affects other refractory metal oxides such as activated alumina. At elevated temperatures, both activated alumina and bulk ceria suffer a reduction in their surface areas and this significantly reduces the effectiveness of the catalyst. It is known to stabilize refractory metal oxides such as alumina and ceria against such thermal degradation. One known technique is to impregnate into bulk 30 alumina a solution of a soluble rare earth metal salt, e.g., a cerium salt such as cerium nitrate, and then calcine the impregnated alumina to provide a ceria-impregnated alumina to stabilize the alumina against thermal degradation. It is similarly known to

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stabilize bulk ceria against thermal degradation by impregnating it with a solution of a soluble aluminum salt such as aluminum nitrate, followed by calcination to provide an alumina-impregnated bulk ceria. Other OSCs can be prepared as co-formed oxides of cerium and at least one other metal such as zirconium. Such co-formed oxides can  
5 comprise a wide range of proportions of ceria to the at least one other metal oxide, e.g., in the range of from about 5 percent ceria upward. For example, co-formed ceria-zirconia oxide may comprise from 10 to 90 percent ceria. Alternatively, a co-formed ceria-zirconia oxide may comprise from about 10 to 50 percent ceria, or from about 10 to 40 percent ceria, or even from about 10 to 30 percent ceria. Oxygen  
10 storage components may be used in automotive catalyst members of the present invention at loadings of from about 0.1 to 4 grams per cubic inch, or from about 0.1 to 1.5 g/in<sup>3</sup>, e.g., from about 0.2 to 1.2 g/in<sup>3</sup>, or, preferably, from about 0.5 to 0.8 g/in<sup>3</sup>.

Example 1 (Typical catalyst member preparation steps)

15 A sample catalyst member was prepared as follows. A washcoat slurry of adsorbent material was prepared from a Beta-zeolite material having a particle size distribution such that a majority of the particles had diameters less than 12 microns. The zeolite material was mixed with water and a colloidal silica binder, in a shear mixer. The resulting suspension was passed through a screen filter gauged at 80 mesh  
20 to remove oversized zeolite particles. The filtered slurry was coated onto a cordierite honeycomb carrier of 1.4 liter volume. The coated carrier was dried and calcined, and had 1.2 g/in<sup>3</sup> of the zeolite adsorbent material undercoat thereon.

25 Two precious metal-containing slurries were prepared for coating as a catalytic material overlayer onto the zeolite undercoat on the carrier. The first slurry comprised four species of particles. The first species was prepared by combining baria- and lanthana-doped alumina particles (having 1.3% lanthana and 0.8% baria by weight, of the respective doped alumina particles) and a palladium nitrate solution in a mixer to deposit the palladium on the alumina. The second species of particles was prepared from a quantity of a "co-formed" ceria-zirconia material. Such "co-formed" material  
30 may be made by any suitable technique such as co-precipitation, co-gelling or the like. One suitable technique is illustrated in the article by Luccini, E., Mariani, S., and Sbaizer, O. (1989) "Preparation of Zirconia-Ceria...in Water With Urea", Int. J. of

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Materials and Product Technology, Vol. 4, No. 2, pp. 167-175, the disclosure of which is hereby incorporated herein as background information. As disclosed starting at page 169 of the article, a dilute (0.1M) distilled water solution of zirconyl chloride and cerium nitrate in proportions to promote a final product of  $ZrO_2$  - 10 mol %  $CeO_2$  5 is prepared with ammonium nitrate as a buffer, to control pH. The solution was boiled with constant stirring for two hours and complete precipitation was attained with the pH not exceeding 6.5 at any stage.

Any other suitable technique for preparing the co-formed rare earth metal oxide-zirconia may be employed, provided that the resultant product contains the rare 10 earth metal oxide dispersed substantially throughout the entire zirconia matrix in the finished product, and not merely on the surface of the zirconia particles or only within a surface layer, thereby leaving a substantial core of the zirconia without rare earth metal oxide dispersed therein. Thus, the zirconium and cerium salts may include chlorides, sulfates, nitrates, acetates, etc. The co-precipitates may, after washing, be 15 spray-dried or freeze-dried to remove water and then calcined in air at about 500°C to form the co-formed rare earth metal oxide-zirconia support.

The co-formed ceria-zirconia support material was combined in a mixer with a solution of amine-solubilized platinum hydroxide and water. These were mixed together, and a cerium nitrate solution was also added. The palladium- and 20 cerium-impregnated alumina particles and the platinum and cerium-bearing ceria/zirconia particles were combined in a ball mill with NiO (the third species of particles), with additional co-formed ceria/zirconia, cerium nitrate, and bulk ceria (the fourth species of particles). The particles were ground until a majority of the particles had a diameter less than 12 microns. Then a solution comprising lanthanum, 25 neodymium, nickel, barium and strontium nitrate solutions was added, and milling was continued for 5 minutes. Additional water was added to bring the first slurry to a solid content suitable for coating onto the adsorbent-coated carrier.

The second platinum group metal-containing slurry was prepared by placing a quantity of co-formed ceria/zirconia in a mixer and adding to it a solution of 30 ammonium solubilized platinum hydroxide to impregnate the particles with the platinum solution. Separately, gamma-alumina was placed in a mixer with a quantity of rhodium nitrate solution, and the two were mixed together to impregnate the

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alumina particles with the rhodium nitrate. The platinum-impregnated ceria-zirconia and the rhodium-impregnated alumina were combined in a ball mill with co-formed ceria/zirconia and were milled until a majority of the particles had a diameter less than 12 microns. Zirconium acetate was included in the slurry during milling.

5 The platinum- and palladium-containing first slurry was coated onto the zeolite-bearing carrier, which was then dried and calcined. Then, the coated carrier was coated with the second slurry, dried, and calcined.

10 The platinum group metals of the first slurry or catalytic bottom coat were present in a Pt:Pd ratio of 0.5:220 and provided a platinum group metal loading of 221.5 g/ft<sup>3</sup> on the monolith. The platinum group metals of the second slurry (catalytic top coat) were present in a Pt:Rh ratio of 1:10, at a loading of 5.5 g/ft<sup>3</sup>, for a total platinum group metal loading on the carrier of 227 g/ft<sup>3</sup>.

The finished catalyst member was designated S-1.

15

### Example 2

A dual layer sample catalyst member was produced by first preparing the catalytic bottom coat slurry. The bottom coat slurry was prepared by separately impregnating quantities of gamma-alumina with a palladium nitrate and an amine-solubilized platinum hydroxide solution, respectively, and then combining the 20 impregnated particles in a ball mill with two additional co-formed ceria-zirconia materials comprising 80% ceria and 12% ceria, respectively. The particles were ground until a majority of the particles had a diameter less than 12 microns. Then, a solution comprising lanthanum nitrate, neodymium nitrate and nickel nitrate was added to the mixture, and milling was continued for 5 more minutes.

25 The top coat slurry comprised rhodium-bearing alumina particles prepared by mixing a quantity of gamma-alumina into a rhodium nitrate solution. The mixture was disposed in a ball mill and was milled with co-formed 12% ceria-88% zirconia material so that a majority of the particles had a diameter less than 12 microns. At that point, zirconium acetate was added and milling was continued for 5 minutes.

30 A honeycomb-type carrier without an adsorbent undercoat was coated with the Pt/Pd catalytic material of the bottom coat slurry, dried and calcined, and was then coated with the rhodium-containing catalytic material of the top coat slurry, dried and

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calcined. The finished catalyst member had a total Pt:Pd:Rh ratio of 3:5:1 and a total platinum group metal loading of 67.5 g/ft<sup>3</sup>, and was designated S-2.

Example 3 (Sample test)

5        Sample catalyst members S-1 and S-2 were tested by placing the catalyst members in the underfloor position of an exhaust system in place of the original catalytic converter in a 2.2 liter, 4-cylinder 1990 passenger automobile and subjecting the vehicle to the FTP cold-start hydrocarbon emissions test described above.

10      The results of a modal of hydrocarbon emissions for each of the catalyst members is set forth in the following TABLE I.

TABLE I  
HYDROCARBON EMISSIONS

15	MODE	TIME (sec)	ENGINE OUT		TAILPIPE	
			Hydrocarbons (ppm)			
			S-2	S-1	S-2	S-1
	I	20	917	1005	1259	276
20	A	12	850	1095	1152	731
	D	8	939	827	852	579
	A	8	697	826	885	582
	D	7	781	721	677	597
	A	8	674	747	593	654
25	C	16	664	704	383	670
	C	36	545	589	147	255
	D	10	584	1116	57	224

30

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TABLE I  
(CONTINUED)

5	<u>ENGINE OUT</u>		<u>TAILPIPE</u>		<u>PERCENT</u>	
	(Modal Grams)				<u>CONVERSION</u>	
	S-2	S-1	S-2	S-1	S-2	S-1
10	0.125	0.133	0.172	0.036	- 37.4%	72.6%
	0.280	0.400	0.379	0.267	- 35.5	33.2
	0.096	0.071	0.087	0.049	9.2	30.1
	0.129	0.158	0.164	0.111	- 27.0	29.6
	0.094	0.090	0.082	0.075	13.4	17.1
	0.146	0.174	0.128	0.152	12.0	12.4
	0.187	0.238	0.108	0.227	42.4	4.9
	0.441	0.510	0.119	0.221	73.0	56.7
15	0.045	0.076	0.004	0.015	90.2	79.9
	—	—	—	—	—	—
TOTALS:		2.284	2.741	1.841	1.709	19.4
		—	—	—	—	37.7

20

I = Idle

A = Acceleration at 2.2 mph/sec

D = Deceleration at (0 3.1) mph/sec

25 C = Cruise

The data in TABLE I show that during three of the first four modes of the test, catalyst member S-2 showed poor catalytic activity, i.e., conversion activity did not keep pace with the desorption into the gas stream of hydrocarbons deposited within 30 the exhaust apparatus from prior tests. In contrast, catalyst member S-1 showed consistent catalytic performance even during the initial stages of the test. In the last three stages of the test, the comparative catalyst member performed better than the

experimental catalyst. This is believed to be due to the fact that the experimental catalyst was by then treating desorbed hydrocarbons as well as those in the exhaust gas stream; the increased volume of hydrocarbons being treated caused the somewhat lower conversion rates. Nevertheless, over the course of the test, the ability of catalyst 5 member S-1 to adsorb hydrocarbons and retain them until the catalytic material reached its light-off temperature yielded a superior conversion performance relative to comparative catalyst member S-2, as reflected in the total modal emission and conversion rates set forth at the bottom of TABLE I.

10

Example 4

A catalyst member comprising a carrier with a three-layer coating thereon including an adsorbent layer undercoat, a barrier layer and a catalytic layer top coat in accordance with the present invention was prepared as follows, and was designated E-1.

15

An adsorbent material was prepared from a mixture of a zeolite powder and a binder, the zeolite comprising about 90% by weight of the mixture. The mixture was mixed into water to form an aqueous slurry having about 38 to 40% solids content.

20

A barrier material was prepared from a combination of cerium compounds including cerium oxide, cerium hydroxide and a co-formed cerium-zirconium-neodymium oxide. The cerium compounds were combined with zirconium and aluminum acetate binder compounds. The co-formed cerium compound, the cerium oxide and the cerium hydroxide were employed in relative weight ratios of 1:3:0.1.

25

A catalytic material comprising palladium-bearing alumina and platinum- and rhodium-bearing alumina was prepared. The palladium-bearing alumina was prepared by impregnating a lanthanum- and barium-stabilized alumina powder with an aqueous palladium solution. Aqueous nitrate salts of lanthanum and neodymium were subsequently added, followed by barium acetate. The impregnated alumina was dried and calcined at 530°C for one hour and was designated the palladium frit ("Pd-frit"). The Pd-frit was milled for 12 hours and formed into a slurry at about 49.5% solids content.

A second frit was prepared by impregnating alumina particles with a solution containing dissolved platinum salts. An aqueous rhodium salt solution was added to

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impregnate the alumina with rhodium as well. Nitric acid was added and the resulting mixture had a solids content of 43.5% and was ball milled for 8 hours to yield a platinum- and rhodium-containing slurry.

5 The palladium-containing slurry and the platinum- and rhodium-containing slurry were then combined to produce a slurry comprising the catalytic material.

A honeycomb-type carrier was coated with the adsorbent material to form a washcoat adsorbent layer having a loading of about 1.2 to 1.3 g/in<sup>3</sup> (dry weight gain). A slurry comprising the barrier material was coated over the adsorbent material, dried and then calcined. The barrier layer had a loading in the range of 1.55 to 1.6 g/in<sup>3</sup> 10 (dry weight gain). The slurry comprising the catalytic material was coated over the barrier layer and was then dried and calcined to yield a catalytic layer at a loading of 1.8 g/in<sup>3</sup> (dry weight gain). The platinum was present at a loading of 9 g/ft<sup>3</sup>, rhodium at 5 g/ft<sup>3</sup> and palladium at 330 g/ft<sup>3</sup>.

15 The finished catalyst member, designated E-1, had three washcoat layers on it as suggested in Figure 1C, the adsorbent layer corresponding to layer 20a', the barrier layer corresponding to layer 20c' and the catalytic layer corresponding to layer 20b'. Catalyst member E-1 was subjected to FTP testing as described above, during which the conversion rates for hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO<sub>x</sub>) were measured. The catalyst member was then subjected to 50 hours 20 engine aging and was then re-tested. The results are set forth in TABLE II.

TABLE II  
Catalyst Member E-1

25	Conversion (%)		
	HC	CO	NO <sub>x</sub>
Fresh	97.6	95.4	99.4
Aged	95.7	91.3	97.9

30	ULEV	Conversion Requirements		
		96.5	95.9	98
	LEV	93.6	91.6	92

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The results of TABLE II show that when fresh, the conversion activity of catalyst member E-1 met the California Air Resources Board (CARB) Ultra Low Emission Vehicle (ULEV) hydrocarbon and NO<sub>x</sub> conversion standards, and that after aging, catalyst member E-1 met the CARB Low Emission Vehicle (LEV) hydrocarbon and NO<sub>x</sub> conversion standards.

Example 5

Three sample catalyst members were prepared: one sample in accordance with an embodiment of the present invention (designated E-2) and two comparative samples (designated C-1 and C-2).

Each of samples E-2, C-1 and C-2 comprised catalytic material prepared as generally described above, comprising palladium and rhodium in a 14:1 weight ratio and coated onto a honeycomb carrier at a weight of 2.9 grams per cubic inch to provide 150 grams of platinum group metals per cubic foot. The catalytic material was applied in two layers: a bottom layer applied at a coating weight of 1.7 grams per cubic inch and comprising alumina support material impregnated with cerium, zirconium, strontium and palladium, and a top layer applied at a coating weight of 1.2 grams per cubic inch and comprising a support phase comprising a mixture of alumina, zirconia and a co-formed ceria-zirconia material impregnated with rhodium.

Sample C-1 comprised only the catalytic material on the carrier. Sample C-2 comprised a hydrocarbon trap layer under the catalytic material. The trap layer was prepared in the same manner and coated in the same way as described in Example 1.

Sample E-2 comprised the catalytic material, the hydrocarbon trap layer and a barrier coat between them. The barrier coat material comprised alumina, a co-precipitated ceria-zirconia material containing 40% ceria, and bulk zirconia, all mixed and milled as described above. No platinum group metals were deposited on the barrier coat material.

Samples E-2, C-1 and C-2 were aged in engine exhaust at 650°C and were then tested for hydrocarbon, carbon monoxide and NO<sub>x</sub> conversion ability. The results are presented in TABLE III.

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TABLE III

<u>Sample</u>	<u>HC</u>	<u>CO</u>	<u>NO<sub>x</sub></u>
	<u>Conversion %</u>	<u>Conversion %</u>	<u>Conversion %</u>
5 C-1	83	64	64
C-2	83	58	64
E-2	84	69	65

The data of TABLE III show that Sample E-2 unexpectedly showed superior resistance to loss in carbon monoxide conversion performance after aging relative to the comparative samples, while maintaining comparable resistance to loss in post-aging hydrocarbon and NO<sub>x</sub> conversion performance. This illustrates the unexpected advantage of using a barrier layer in accordance with the present invention.

15

Example 6

In another series of tests, a catalyst member in accordance with the present invention (designated E-3) was compared against three comparative catalyst members (designated C-3, C-4 and C-5).

Sample catalyst member E-3 comprised a catalytic material that provided 150 grams of palladium and rhodium per cubic foot, in a 14:1 weight ratio, and was applied in two layers as described in Example 5. It included a hydrocarbon trap layer comprising a Beta-zeolite adsorbent under the catalytic material and an alumina barrier layer therebetween.

Comparative sample C-3 was prepared in a manner similar to sample E-3, but without the barrier layer; sample C-4 was prepared similarly as well, but without either a barrier layer or hydrocarbon trap layer.

Sample C-5 comprised a catalytic material comprising platinum, palladium and rhodium in a weight ratio of 1:25:3, applied in two coats to provide a total of 153 grams per cubic foot of platinum group metals. It did not include a hydrocarbon trap layer or barrier layer.

Samples E-3, C-3, C-4 and C-5 were tested fresh and after engine aging for hydrocarbon, carbon monoxide and NO<sub>x</sub> conversion. Sample E-3 showed

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significantly less loss in conversion performance than sample C-3, demonstrating that having a barrier layer in accordance with the present invention between a hydrocarbon trap layer and a catalytic material yields an unexpected benefit with regard to the long-term hydrocarbon conversion performance. Samples C-4 and C-5, which did not 5 include a hydrocarbon trap layer, showed less loss of conversion performance after aging than samples C-3 and E-3, illustrating that the hydrocarbon trap layer appears to have a detrimental effect on the catalytic material, and that the barrier layer of the present invention unexpectedly ameliorates this effect.

10 While the invention has been described in detail with reference to a particular embodiment thereof, it will be apparent that upon a reading and understanding of the foregoing, numerous alterations to the described embodiment will occur to those skilled in the art and it is intended to include such alterations within the scope of the appended claims.

15

THE CLAIMS

What is claimed is:

- 5        1. A catalyst member suitable for catalyzing the conversion to innocuous substances of at least gaseous hydrocarbons contained in an oxygen-containing exhaust stream, the catalyst member comprising:
  - a refractory carrier;
  - an adsorbent layer disposed on the carrier and comprising an adsorbent material for adsorbing hydrocarbons at temperatures up to a desorption temperature  $T_D$ ;
  - a permeable barrier layer disposed over the adsorbent layer; and
  - 10        a permeable catalytic layer disposed over the adsorbent layer and the barrier layer and comprising a catalytic material effective at least for the conversion of hydrocarbons to innocuous substances.
- 15        2. The catalyst member of claim 1 wherein the barrier layer comprises alumina.
- 20        3. The catalyst member of claim 1 wherein the barrier layer comprises an oxygen storage component.
- 25        4. The catalyst member of claim 1 wherein the barrier layer comprises alumina and an oxygen storage component.
- 30        5. The catalyst member of claim 4 wherein the barrier layer comprises bulk ceria.
- 35        6. The catalyst member of claim 4 wherein the barrier layer comprises ceria impregnated into the alumina.

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7. The catalyst member of claim 4 wherein the barrier layer comprises a co-formed oxide comprising ceria and at least one other metal oxide.

8. The catalyst member of claim 7 wherein the co-formed oxide comprises  
5 ceria and zirconia.

9. The catalyst member of claim 7 wherein the co-formed oxide comprises at least about 5 percent ceria.

10 10. The catalyst member of claim 7 wherein the co-formed oxide comprises from about 10 to 50 percent ceria.

11. The catalyst member of claim 10 wherein the co-formed oxide comprises from about 10 to 40 percent ceria.

15 12. The catalyst member of claim 11 wherein the co-formed oxide comprises from about 10 to 30 percent ceria.

13. The catalyst member of claim 4 wherein the barrier layer comprises  
20 alumina stabilized with at least one alkaline earth metal oxide.

14. The catalyst member of any one of claims 1, 2, 3, 7 or 13 wherein the barrier layer is substantially free of platinum group metals.

25 15. The catalyst member of any one of claims 1, 2, 3, 7 or 13 having a light-off temperature  $T_L$  which is not more than about 150°C higher than the desorption temperature  $T_D$ .

16. The catalyst member of claim 15 wherein the light-off temperature  $T_L$  is not  
30 more than about 50°C higher than the desorption temperature  $T_D$ .

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17. The catalyst member of claim 16 wherein the light-off temperature  $T_L$  is not higher than the desorption temperature  $T_D$ .

18. The catalyst member of any one of claims 1, 2, 3, 7 or 13 wherein the 5 catalytic material comprises a platinum group metal component dispersed on a refractory metal oxide support material in an amount of at least about 100 grams of at least one platinum group metal per cubic foot of the catalyst member.

19. The catalyst member of claim 18 wherein the catalytic material comprises 10 the at least one platinum group metal in the amount of from about 200 to 700 grams per cubic foot of the catalyst member.

20. The catalyst member of claim 19 wherein the catalytic material comprises more than 300 grams of the at least one platinum group metal per cubic foot of the 15 catalyst member.

21. The catalyst member of claim 1 wherein the adsorbent layer comprises a Beta-zeolite material having a Si:Al atomic ratio of at least about 100.

20 22. A method for reducing hydrocarbon emissions in the exhaust gas of an internal combustion engine, at least during a cold-start period of engine operation, comprising flowing the exhaust gas through an exhaust system comprising the catalyst member of any one of claims 1, 2, 3, 7 or 13.

[received by the International Bureau on 1 October 1999 (01.10.99);  
original claim 22 cancelled; original claims 20 and 21 amended;  
new claims 23-27 added; remaining claims unchanged (2 pages)]

17. The catalyst member of claim 16 wherein the light-off temperature  $T_L$  is not higher than the desorption temperature  $T_D$ .

18. The catalyst member of any one of claims 1, 2, 3, 7 or 13 wherein the catalytic material comprises a platinum group metal component dispersed on a refractory metal oxide support material in an amount of at least about 100 grams of at least one platinum group metal per cubic foot of the catalyst member.

19. The catalyst member of claim 18 wherein the catalytic material comprises the at least one platinum group metal in the amount of from about 200 to 700 grams per cubic foot of the catalyst member.

20. The catalyst member of claim 18 wherein the catalytic material comprises more than 300 grams of the at least one platinum group metal per cubic foot of the catalyst member.

21. The catalyst member of claim 1 wherein the adsorbent layer comprises a Beta-zeolite material having a Si:Al atomic ratio of at least about 100:1.

22. Canceled.

23. The catalyst member of claim 1 wherein the barrier layer comprises one or more of alumina, foamed alumina, zirconia, lanthana, yttria, neodymia, and any one or more alkaline earth metal oxides.

24. The catalyst member of claim 23 wherein the barrier layer is substantially free of platinum group metals.

25. The catalyst member of claim 1, claim 23 or claim 24 wherein the barrier layer is substantially free of silicon.

26. The catalyst member of any one of claims 2-7 or 9-13 wherein the barrier layer is substantially free of silicon.

27. A method for reducing hydrocarbon emissions in the exhaust gas of an internal combustion engine, at least during a cold-start period of engine operation, comprising flowing the exhaust gas through an exhaust system comprising the catalyst member of any one of claims 1, 2, 3, 7, 13, 23 or 24.

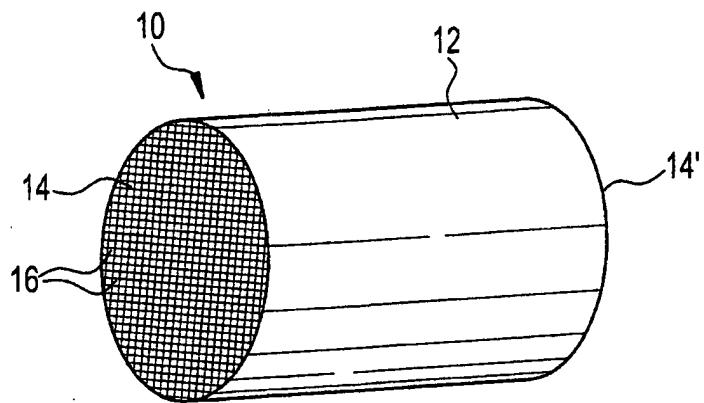
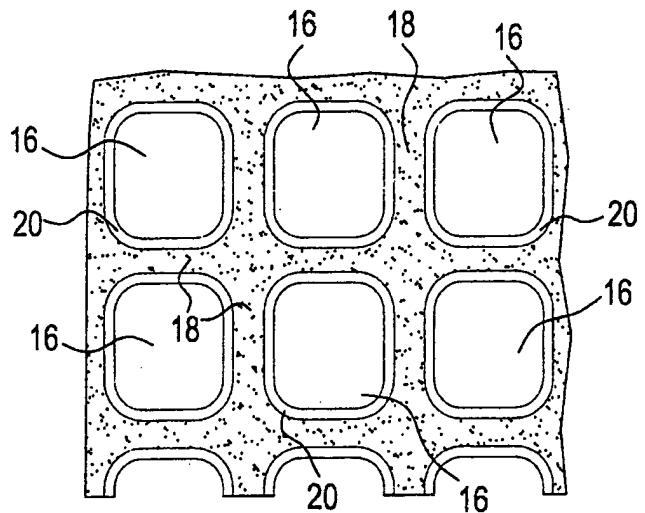
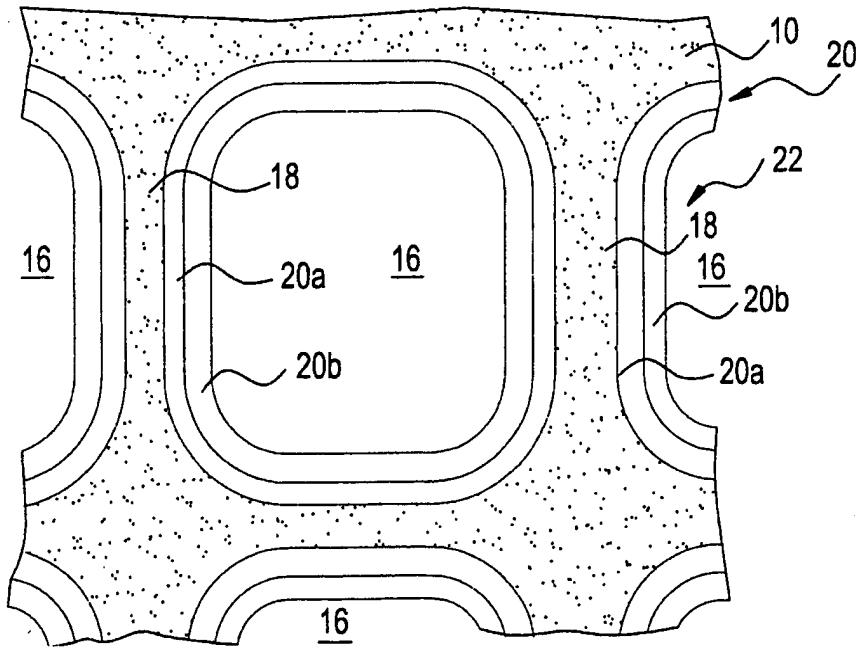
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**FIG.1****FIG.1A****FIG.1B**

FIG.1C

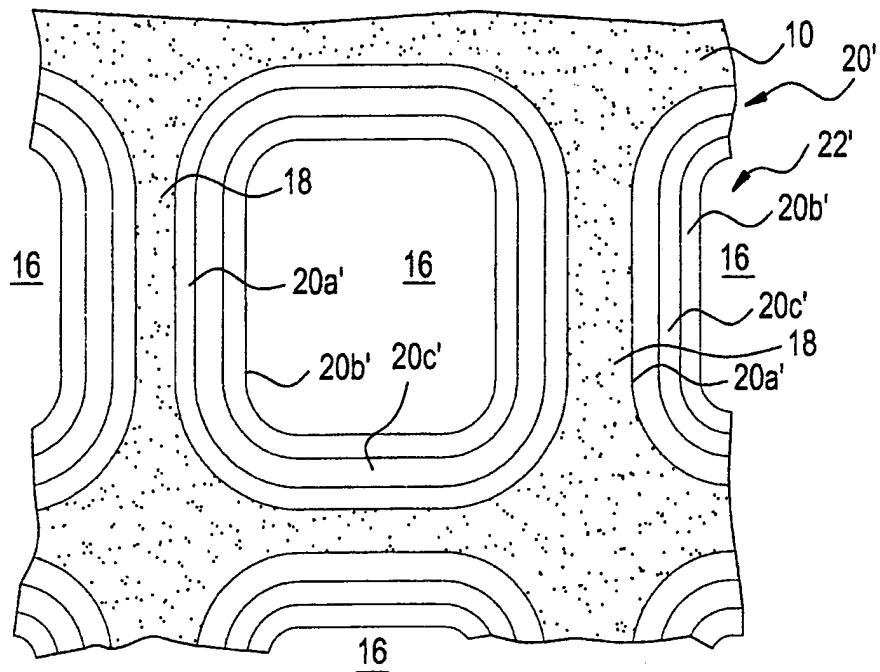
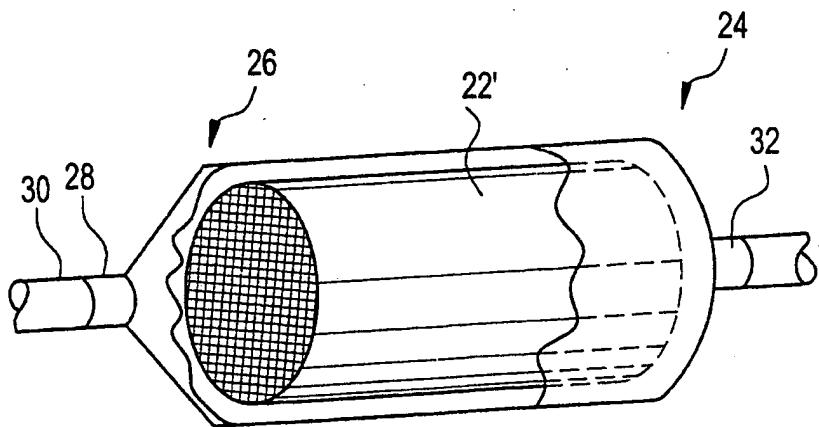


FIG.2



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